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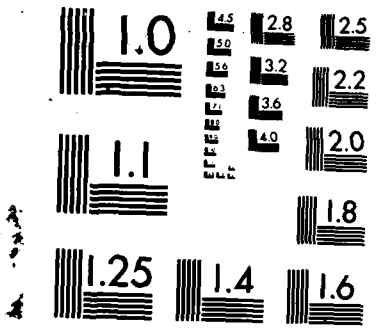

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AN ELECTROCHEMICAL EVALUATION OF MICROBIOLOGICALLY INDUCED CORROSION BY TWO IRON-OXIDIZING BACTERIA

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ABSTRACT

The anodic corrosion current resulting from the colonization of carbon steel and nickel electrodes by an heterotrophic iron-oxidizing bacterium was 10.4 μA/cm² and 0.1 μA/cm², respectively, indicating that oxidation reactions controlled the overall corrosion. Both metals were shown to be electrochemically active in the presence of differential aeration and acidic metabolites. Accumulations of ferric hydroxide on the surface of the carbon steel resulted in an anodic current of 8.6 μA/cm² that persisted after the colonizing microorganisms had been heat-killed.

Attempts were made to measure the electrochemical impact of an autotrophic iron-oxidizing bacterium on the corrosion of stainless and carbon steels in the presence and absence of added soluble $Fe^{(++)}$. Under the experimental conditions described, it was impossible to demonstrate microbiologically induced corrosion with these microorganism/substrata combinations.

INTRODUCTION

An iron-oxidizing bacterium capable of obtaining energy from iron was first identified by Colmer and Hinckle in 1947.[1] The organism, Thiobacillus ferroxidans, was described as an obli-

gate autotrophic bacterium that could transport reduced iron into the cell, oxidize it to the ferric state, and transport it out of the cell. Heterotrophic iron-oxidizing bacteria have also been described that are capable of using certain organic compounds in addition to reduced iron to meet energy needs.[2,3]

Our knowledge of iron metabolism is less than complete. Iron is known to be a component of respiratory enzymes, such as the heme-containing compounds, and iron storage compounds such as ferritin, ferrichrome. Electron transport through cytochrome c and cytochrome a to oxygen yields ATP which can be used for the generation of DPNH and cell synthesis. However, the low energy yield (11.3 kcal/g-atom) of the reaction:

$$Fe^{++} \longrightarrow Fe^{+++} + e^{-}$$

requires that large quantities of iron must be processed to meet the cell energy requirements. The capacity to oxidize iron and the requirement for large quantities make iron-oxidizing bacteria of particular interest in the study of microbiologically induced corrosion of iron-containing materials. The electrochemical impact of both a heterotrophic and an autotrophic iron-oxidizing bacterium was evaluated using steel electrodes in a dual electrode system.

METHODS AND MATERIALS

Bacteria

The bacterium tentatively identified as Thiobacillus ferroxidans was isolated from coal mine effluent, pH 5.6, taken from Ella Hollow, Pennsylvania, containing both reduced sulfur and iron compounds. Standard microbiological techniques were used to isolate and maintain pure cultures in the medium described by Beck[4] to which no organic carbon was added. The electrochemical impact of this isolate was evaluated using stainless steel (Allegheny-Ludlum 6X) and carbon steel electrodes in the Beck medium with and without the addition of Fe^{++}. The heterotrophic iron-oxidizing bacterium was isolated from a corroding carbon-steel water box that had been filled with naturally occurring estuarine water ($3^{o}/oo$). The isolate was maintained in a minimal broth supplemented with 0.025% each tryptone and yeast extract.[5] The electrochemical impact of the heterotrophic iron-oxidizing bacterium was evaluated on carbon steel and nickel 201 electrodes in that medium.

Corrosion experiments

A schematic diagram of the corrosion-measuring device described elsewhere[5] is presented in Figure 1. Duplicates of either acetone-cleaned

carbon steel, stainless steel, or nickel 1-cm^2 electrodes were placed into the compartments with the previously described media. The entire assemblage was autoclaved for 15 min at 120°C and 15 psi. One flask of the cell was inoculated with a disc of the same composition previously colonized by microorganisms, while a sterile disc was dropped into the flask to be kept in an abiotic condition. The electrodes were then galvanically coupled and the resulting currents measured with an EG&G PARC corrosion measuring device (Model 350).

In such a system the measuring device functions as a zero resistance ammeter; i.e., the potential of the galvanic cell is not perturbed by the current measurements. If the identical metal specimens are galvanically coupled and are isolated in identical electrolyte solutions, the current flow between them is zero, even in the presence of active corrosion. They corrode at the same rate and neither functions as an anode or cathode in reference to the other. If this balance is disturbed by the presence of colonizing microorganisms, a current flows between the two specimens. If the reaction that is taking place at the surface of the inoculated electrode is an oxidation, an anodic current will be recorded; if it is a reduction, a cathodic current will result.

In addition to the experiments with the bacterial isolates, experiments were designed to abiotically test the individual effects of bacterial respiration and acid metabolite production on the corrosion of metal substrata. In the abiotic experiments the 0.1 μm Millipore filter was replaced with a Teflon disc to ensure chemical separation of the two compartments. A KCl/agar bridge maintained electrolytic conductivity.

RESULTS AND DISCUSSION

In all cases the specimen in the cell inoculated with the heterotrophic iron-oxidizing bacterium became the anode of the galvanic couple, indicating that an oxidation reaction was, in fact, controlling the overall corrosion. However, a range of currents was observed, depending on the organism, the substratum, and the chemical composition of the electrolyte.

Colonization of a carbon steel electrode by the heterotrophic iron-oxidizing bacterium resulted in an anodic current of 10.4 μA cm^{-2} (Figure 2) after a 40-hour incubation. No ferrous iron was added to the electrolyte, so that any accumulations of red ferric iron deposits were the result of an oxidation of the electrode. At physiological pH values, both electrodes undergo spontaneous oxidation which provides a source of Fe^{++} for organisms. Since spontaneous oxidation takes place on both galvanically coupled electrodes, it does not contribute to the net current. The

microbial oxidation of Fe^{++} to Fe^{+++} resulted in large red deposits that covered 75% of the surface of the electrode. The corrosion current measured after the microorganisms were heat-killed was 8.6 $\mu A\ cm^{-2}$, demonstrating that the accumulated ferric hydroxide created differential aeration cells that were independent of the biochemical activity of the bacteria. Dense accumulations of ferric hydroxide prevent the diffusion of oxygen producing a voltage drop. Any geometrical factor that results in a higher concentration of oxygen at one part of a metal surface and a lower or zero concentration at another will result in the former becoming the cathode and the latter the anode of the corrosion cell. Such deposits encourage hydrolysis reactions that concentrate chlorides and create acid environments that prevent passivation and further contribute to anodic currents (Figure 3).

Iron-oxidizing bacteria are efficient scavengers of dissolved oxygen, so that respiration creates localized concentration cells similar to those previously described. This situation was simulated abiotically. Under sterile conditions, oxygen was bubbled through both compartments of the cell containing carbon steel electrodes. The current between the two compartments was zero. Differential aeration was created by replacing the oxygen in one of the compartments with nitrogen. Differential aeration created an anode of the carbon steel electrode exposed to nitrogen.

Heterotrophic iron-oxidizing microorganisms can impact metal corrosion in other ways. Most heterotrophic bacteria secrete organic acids during the fermentation of organic substrates that have been shown to cause corrosion.[7,8] The types and amounts of acids produced in nature depend on the kinds of organisms present and the substrate molecules available. However, in natural microaerobic habitats, acetic acid is a major organic acid produced. The electrochemical impact of 10 mM acetic acid on carbon steel was 7.54 $\mu A\ cm^{-2}$.

Because heterotrophic iron-oxidizing bacteria can impact corrosion via a number of different mechanisms, their presence on metal substrata other than those containing iron may enhance corrosion. This was demonstrated by inoculating one compartment of the dual electrode cell containing equilibrated nickel electrodes with the iron-oxidizing bacteria. No Fe^{++} was provided in the electrolyte. The anodic corrosion current stabilized at 0.1 $\mu A\ cm^{-2}$. Nickel is a metal that forms a passivating film under alkaline conditions and has been shown to be susceptible to attack induced by acidic metabolites and to differential aeration.[5]

The autotrophic iron-oxidizing bacterium was exposed to stainless and

carbon steel electrodes in the presence and absence of Fe^{++} ions in solution and the resulting corrosion currents measured. In the presence of Fe^{++} ions in the electrolyte, the solution changed from a clear solution to a turbid orange one with accumulations of iron and sulfur on the electrode surface and at the air-water interface. In the absence of added Fe^{++} ions, the solution color changed slightly; however, microorganisms could not be found on the exposed electrode surface using scanning electron microscopy. Corrosion current remained near zero for all of the experimental conditions.

CONCLUSIONS

Heterotrophic iron-oxidizing microorganisms enhanced the corrosion of carbon steel and nickel electrodes in the absence of soluble Fe^{++}. Tubercules of ferric hydroxide on the carbon steel created under-deposit corrosion that was independent of the biochemical activity of the cells.

Under the experimental conditions described, it was impossible to demonstrate microbially induced corrosion of stainless steel or carbon steel by an obligate autotrophic iron-oxidizing microorganism.

ACKNOWLEDGEMENT

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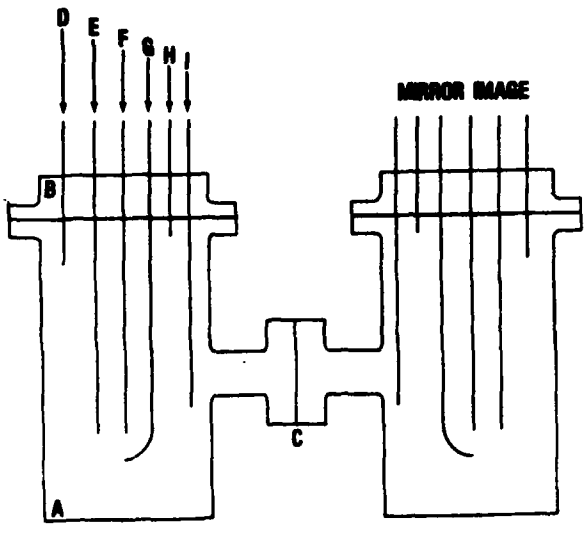


A - HALF CELL
B - CELL COVER
C - MEMBRANE
D - UTILITY PORT
E - PT ELECTRODE
F - METAL SPECIMEN
G - LUGGIN CAPILLARY
H - GAS OUTLET
I - GAS INLET

Figure 1. Corrosion-measuring device.

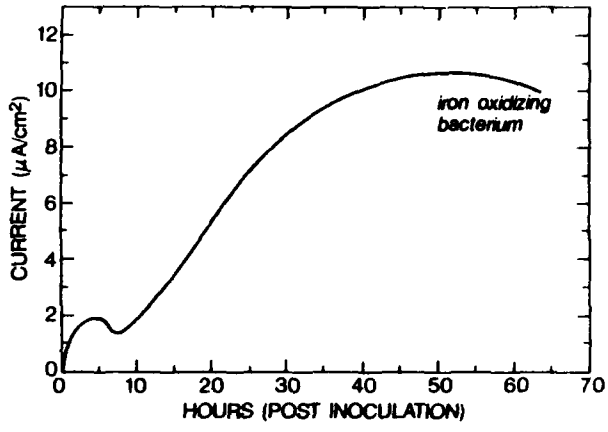


Figure 2. Corrosion current vs. time resulting from colonization of carbon steel.

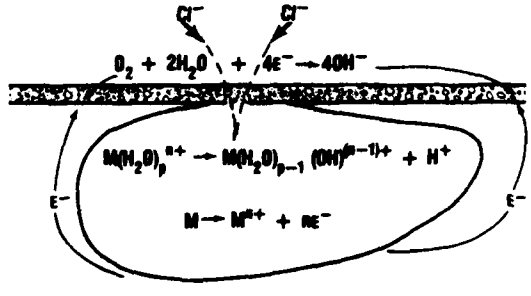
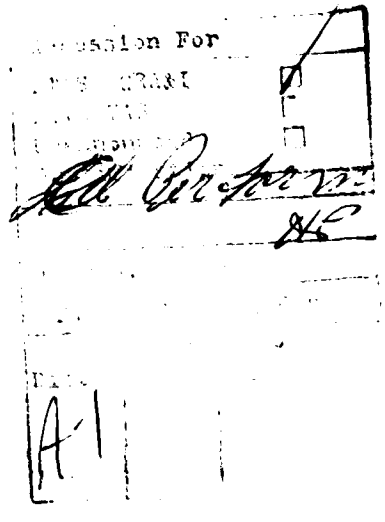


Figure 3. Schematic diagram of pit initiation.



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